Investigation of the Transfer Function between Atmosphere and Snow Concentrations of Hydrogen Peroxide at South Pole

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Oxidation by OH is the main atmospheric sink for many environmentally important gases including methane (CH₄), carbon monoxide (CO), and halogenated hydrocarbons involved in stratospheric ozone depletion. With a very short lifetime, OH is not preserved in snow and ice. Hydrogen peroxide (H₂O₂) is a sink for OH, and, because H₂O₂ is preserved in polar snow, firn, and ice, an ice core record of H₂O₂ is potentially a proxy for changes in atmospheric OH through time. In addition, recent springtime depletion of stratospheric ozone has changed the level of solar radiation in the lower troposphere over Antarctica, thereby changing tropospheric photochemistry and also the chemistry of the surface and near-surface snow. However, deposition of H₂O₂ from the atmosphere to the near-surface snow and firn is reversible; some fraction of the originally deposited mass cycles between the atmosphere and the snow as the snow ages and is buried while environmental conditions change. The result is an atmosphere-to-snow transfer relationship that is highly nonlinear with temperature, as well as accumulation rate and accumulation timing. Our research is aimed at better understanding this transfer relationship and developing physically based numerical models of the transfer processes. The eventual goal is to quantitatively invert the ice core record to an atmospheric record of H₂O₂ and provide constraints on past OH concentration.

Field and modeling studies are conducted at a number of remote locations in the arctic and antarctic. The objective is to develop information on H₂O₂ transfer and preservation in as many depositional environments as possible for use in model development and validation. Current antarctic study sites are shown in Figure 1. South pole is the key site for detailed process level studies because of a long record of high quality atmospheric and meteorological measurements, year round occupation, low mean annual temperature, and relatively high accumulation rate. Through our cooperative agreement with CMDL, surface and near-surface snow samples have been collected since November 1994. Replicate snow samples are collected by CMDL staff approximately once each week throughout the year and shipped back to our laboratories in Tucson and Reno for chemical determinations. The record of H₂O₂ concentration in surface snow at south pole (Figure 2) shows a highly repeatable annual cycle with a distinct peak in mid-November of each year, well before the summer solstice. Efforts to understand and model both surface and near-surface snow concentrations at south pole have been described previously [McConnell, 1997; McConnell and Bales, 1998; McConnell et al., 1997, 1998, 1999; Stewart and McConnell,

Collaboration with CMDL staff at the south pole continues under NSF grants 9903744 and 9811875. Five shallow firn cores were collected in 1999 and 2000 within 15 km of the station.

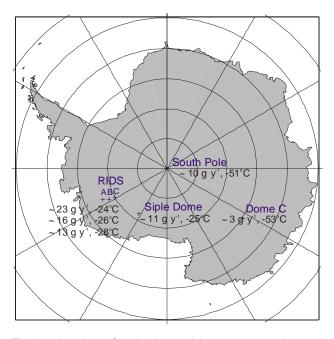


Fig. 1. Locations of study sites used by current atmosphere-snow transfer modeling. Also shown are the mean annual snow accumulation rates and air temperatures.

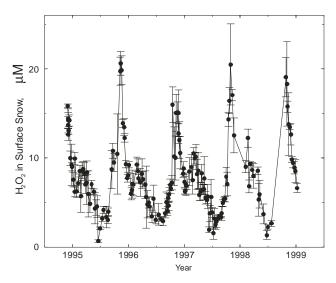


Fig 2. Hydrogen peroxide in surface snow at south pole. Error bars show one standard deviation in replicate measurements.

Three of these cores were sectioned and analyzed for H_2O_2 and formaldehyde (HCHO) on site at the Atmospheric Research Observatory (ARO). Formaldehyde, a highly volatile, photochemically linked atmospheric chemical species, is also preserved in snow and ice. Preliminary field and modeling results of HCHO transfer and preservation were reported by *Hutterli et al.* [1999]. An atmospheric H_2O_2 detector was installed in ARO and maintained for much of the 1999/2000 summer field season under the supervision of CMDL staff.

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